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Importance of volatile organic compounds photochemistry over a forested area in central Greece

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Abstract

The impact of biogenic volatile organic compound (BVOC) on the chemical composition of the boundary layer in a valley-forested site of central Greece is investigated by using a chemical box model able to simulate α - and β -pinene and isoprene photochemistry in the troposphere. The model assimilates the meteorological conditions and mixing ratios of long-lived species observed during the AEROBIC field campaign in July–August 1997. Only 23–61% of the observed ozone (O_3) mixing ratios can be attributed to the local photochemistry during the first part of the experiment, whereas this contribution increases to 80–96% during the second part of the campaign. The remaining part of O_3 is reaching the boundary layer mainly from the free troposphere during the morning opening of the valley. The local net photochemical production of O_3 is calculated to be up to 10 ppbv h^{-1} , up to 60% of which is attributed to BVOC chemistry. BVOC oxidation is also shown to be an important source of carbon monoxide (CO) producing $1.5\text{--}2.5 \text{ ppbv CO h}^{-1}$, carbonyl compounds and organic acids in particular contributing by about 1.5–4.3, 0.2–1.1 and 0.1–1 ppbv to the daytime ambient levels of formaldehyde, acetone and formic acid, respectively. BVOC oxidation is also able to produce about $1.3 \mu\text{g m}^{-3}$ ($0.3\text{--}2.5 \mu\text{g m}^{-3}$) of secondary organic aerosol (SOA) that is 9–38% of the observed total organic aerosol levels. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the troposphere, the photodissociation of nitrogen dioxide (NO_2) is at the origin of the photochemical formation of O_3 , which is enhanced in the presence of volatile organic compounds (VOC). During their oxidation, VOC form significant amounts of peroxy radicals (RO_2) in complex chemical reaction sequences initiated by hydroxyl (OH) and nitrate (NO_3) radicals and O_3 itself. The produced RO_2 radicals accelerate the conversion of nitrogen oxide (NO) to NO_2 , reaction of great importance for tropospheric chemistry since NO_x ($\text{NO} + \text{NO}_2$) is emitted into the atmosphere mainly in the form of NO. VOC oxidation also forms organic

acids that can significantly contribute to the acidity of the precipitation and their heavier homologues could act as condensation nuclei in the marine atmosphere (Kawamura and Usukura, 1993). The oxidation of some VOC like terpenes, sesquiterpenes and aromatics can produce low volatility compounds, which condense onto particles or form new ones. These VOC are therefore precursors of secondary aerosols in the troposphere. VOC oxidation also forms carbonyls known for their potential toxicity. Carbonyls can photolyse and produce free radicals, form stable atmospheric products and interact in smog cycles. In particular, acetone has been proposed to significantly contribute to the HO_x budget in the upper troposphere (Singh et al., 1995). The observed unusually high levels of these compounds in the boundary layer and the free troposphere are supporting their potentially great importance on tropospheric chemistry and indicate the lack of sufficient

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information on their sources (Singh et al., 1995; Jaegle et al., 2001).

Areas receiving high solar radiation like the Mediterranean are subject to intensive photochemical reactions leading to oxidant and aerosol build up. Indeed, high O_3 and aerosol loadings have been observed in the Mediterranean (Mihalopoulos et al., 1997; Kouvarakis et al., 2000, 2002a, b; Kourtidis et al., 1996; Millán et al., 1997) where anthropogenic emissions of central and west Europe meet with local natural ones. NO_x is mainly emitted by human activities, whereas, on a global scale, VOC are by almost 90% of natural origin (Guenther et al., 1995; Olivier et al., 1996). The contribution of biogenic sources of ozone and aerosol (organics and sulphate) precursors relative to the anthropogenic ones remains to be determined in particular for the eastern Mediterranean where appropriate studies are very limited. In addition, the effect of long-range transport relative to the local sources of pollutants requires further investigation.

In forested areas, where the concentrations of BVOC are high, BVOC effect on ozone and OH concentrations becomes significant. Vegetation emits numerous BVOC, but mainly isoprene (C_5H_8) and terpenes (α -pinene, β -pinene and homologues), together with carbonyl compounds like acetone (Guenther et al., 1995). Terpenes, globally emitted by vegetation in amounts 3 times lower than isoprene (Guenther et al., 1995), are very reactive as isoprene. In the atmosphere, some of their oxidation products have low vapour pressure and therefore can condense onto the pre-existing particles or even form new ones. These particles can scatter solar radiation, act as condensation nuclei and even cloud condensation nuclei and affect climate. Their surface can also accommodate heterogeneous reactions.

To investigate the 'in situ' formation of ozone, oxygenated compounds like aldehydes and organic acids and aerosols in a forested area around the Mediterranean and to elucidate the impact of BVOC on the local tropospheric chemistry via gas and particulate phase

reactions, a field experiment has been performed at a forested site in central Greece in summer 1997. The experiment was part of the 'AEROSol formation from BIogenic organic Carbon' (AEROBIC) EU-financed program. Detailed studies of the aerosol and gas-phase chemical composition of the atmosphere have been performed (Bonsang et al., 1999; Kavouras et al., 1998, 1999; Harrison et al., 2001).

An up-to-date chemical box model is used here to simulate VOC impact on tropospheric chemistry at this forested site of central Greece. This work complements the earlier published studies (Carslaw et al., 2001; Creasey et al., 2001) using AEROBIC-1997 data since it focuses on VOC impact on O_3 , HO_x , light organic acids, carbonyls and SOA.

2. The model

The chemical box model developed for the present study uses the FACSIMILE software suitable for the integration of stiff chemical reactions (AEA Technology, 1994). The model includes several hundreds of gas-phase reactions (Tsigaridis, 2000) and a few critical heterogeneous ones (Table 1). The VOC oxidation scheme is based on the most recent kinetic data, both for reaction rates and products when available, and the closest approximation when experimental data are missing. The related uncertainties and their impact on the model results are major points of discussion. A spin-up time of 4 days (needed by the model to reach dynamic equilibrium) has been used for all simulations.

2.1. Chemical mechanism

The model is based on the reduced chemical scheme constructed by Poisson et al. (2000) to describe C_1 – C_5 hydrocarbon oxidation chemistry (methane (CH_4), ethane and ethene (C_2H_6 and C_2H_4), propane and propene (C_3H_8 and C_3H_6), *n*-butane (n - C_4H_{10}) and

Table 1

Heterogeneous reactions taken into account in the model. The loss rate is calculated based on the reactive uptake coefficient (γ) given in the table and by the following expression (Ravishankara, 1997): $k = \omega A \gamma / 4$, where ω is the mean molecular speed of the species of interest (in $cm\ s^{-1}$) and A the reactive surface area for reaction in $cm^2\ cm^{-3}$ and T is the temperature in Kelvin

Reaction	Reactive uptake coefficient (γ)	Reference
$NO_2 + \text{aerosol carbon} \rightarrow \text{HONO}$	3.3×10^{-4}	http://www.iupac-kinetic.ch.cam.ac.uk
$OH \rightarrow \text{products on particulate phase}$	$4.8 \times 10^{-5} \exp(1750/T)$	Carslaw et al. (1999)
$HO_2 \rightarrow 0.5\ H_2O_2$	0.93	Carslaw et al. (1999)
Jacob (2000)		
$NO_3 + H_2O (aq) \rightarrow HNO_3 + OH$	0.004	Demore et al. (1997)
Jacob (2000)		
$N_2O_5 \rightarrow \text{products on particulate phase}$	0.003	Jacob (2000)
$CH_3O_2 \rightarrow \text{products on particulate phase}$	0.004	Carslaw et al. (1999)

C_5H_8). The chemistry of *iso*-butane has been lumped into the n - C_4H_{10} chemical scheme, and C_5H_8 is represented by a lumped scheme evaluated and tested for forested areas by Poisson et al. (2000, 2001). The model uses the latest kinetic data (DeMore et al., 1997; Atkinson, 1994, 1997; Wallington et al., 1992, 1997) and is extended by about 600 chemical reactions to include α - and β -pinene oxidation chemistry (Tsigaridis, 2000). Reactions with OH and NO_3 radicals and O_3 have been taken into account according to the general oxidation scheme of VOC (Atkinson, 1997). To be valid for both polluted and clean atmospheres, the chemical scheme includes reactions both with NO_x and HO_x . To construct the detailed oxidation scheme for α - and β -pinene many assumptions were necessary due to lack of kinetic data, especially with regard to those other than the initial oxidation steps. For instance, the reactions of the RO_2 radicals proceed via NO addition only for the first generation RO_2 radicals, except when $RONO_2$ products from the second RO_2 generation have been reported in the literature. The radical–radical reactions ($RO_2 + R'O_2$) are assumed to proceed only with CH_3O_2 , which dominates even in a forested area where VOC contribution is elevated (Poisson et al., 2001). In the absence of published experimental data for reactions initiated by O_3 and NO_3 , the oxidation rate of the species that is structurally most similar to the considered one has been used. For OH reactions when experimental data were missing the structure–activity relationship (SAR) introduced by Atkinson (1987) and extended by Kwok and Atkinson (1995) was applied.

The rates of α - and β -pinene reactions with OH, O_3 and NO_3 radicals used in the model are taken from Atkinson (1997). All other observed BVOC have been lumped to α - and β -pinene by increasing appropriately the concentrations of α - and β -pinene as well as their reactivity against OH, O_3 and NO_3 to equal the weighted mean reactivity of the BVOC mixture calculated on the basis of the observed abundances of the various BVOC. Aromatics observed during the experiment (Harrison et al., 2001) are similarly lumped to n - C_4H_{10} , which is used as surrogate for the higher NMHC of anthropogenic origin (Poisson et al., 2000). Aerosol formation from the oxidation of these anthropogenic hydrocarbons is neglected in our study. The thus-performed simulation will be further referred as “basic” simulation. The lumping of i - C_4H_{10} to n - C_4H_{10} is expected to introduce a maximum underestimate of the production rate of acetone by 2 pptv h^{-1} , derived from the observed i - C_4H_{10} levels and assuming a maximum acetone yield of unity on a molar basis.

2.2. Input parameters

The sampling campaign took place at Pertouli, a forested site at 1300 m elevation in central Greece

($39^\circ 54'N$, $21^\circ 44'W$), as part of the AEROBIC EU-financed program in the summer of 1997 (Bonsang et al., 1999; Harrison et al., 2001). Among the four 48 h intensive sampling periods of the experiment, the three with sufficient number of measurements available are considered in the present study. These cover the period (local time) from 27 July 06:00 to 29 July 06:00 (1st intensive), from 30 July 06:00 to 01 August 06:00 (2nd intensive) and from 03 August 06:00 to 05 August 06:00 (3rd intensive). High solar intensity and only few scattered clouds characterised these days. The temperature varied between minimum values of 5 – $7^\circ C$ during night and maximum values of 20 – $23^\circ C$ during day. The main difference between the three intensive periods was a decline in humidity from about 1 – 2% during the first intensive to 0.5 – 1.5% during the third one (Bonsang et al., 1999). Another difference, less evident but important for O_3 efficiency production, is the abundance of NO_x and carbon gases. NO levels were elevated during the 2nd and 3rd intensives, whereas only during the 2nd intensive NO was accompanied by exceptionally high CO and VOC levels.

Hourly mean observations of temperature, of photodissociation frequencies of O_3 (JO^1D) and NO_2 (JNO_2) and of the mixing ratios of H_2O , H_2O_2 , O_3 , NO, NO_2 , CO, C_2H_6 , C_2H_4 , C_3H_8 , C_3H_6 , n - C_4H_{10} , i - C_4H_{10} , isoprene, α - and β -pinene are used as input to the model every hour (Bonsang et al., 1999; Harrison et al., 2001). Due to their short lifetime during the day, NO, NO_2 and non-methane VOC concentrations are forced to the hourly mean observed values every 10 min. This time period is smaller than the shorter lifetime of NO_2 calculated by our model for the experimental daytime conditions. The assimilation by the model of the observed concentrations allows consideration of emissions, deposition and transport of the long-lived species in the model. It is valid when transport is not rapid, as in the present study, since the wind speed was below 3 m s^{-1} during the studied period.

In the beginning of each run, initial concentrations are adopted for CH_4 (1.8 ppmv , parts per million per volume), acetone (CH_3COCH_3 , 0.5 ppbv , parts per billion per volume), formaldehyde ($HCHO$, 2 ppbv), acetaldehyde (CH_3CHO , 0.1 ppbv), nitric acid (HNO_3 , 0.1 ppbv) and for organic particulate material ($4.5 \mu\text{g m}^{-3}$). Because the time resolution of formic ($HCOOH$) and acetic (CH_3COOH) acids measurements (3 – 6 h samplings, Lemonakis, 1999) does not allow to correctly take into account their primary emissions in the model on the basis of the measured mixing ratios, emission rates of $0.7 \text{ nmol m}^{-2} \text{ min}^{-1}$ for formic acid ($1 \text{ nmol} = 10^{-9} \text{ mol}$) and $1.45 \text{ nmol m}^{-2} \text{ min}^{-1}$ for acetic acid (Kesselmeier et al., 1998) are used. Due to lack of observations of acetone during the AEROBIC experiment, no direct emissions of acetone have been considered in our study although acetone has primary

emissions from vegetation (Kesselmeier and Staudt, 1999), which could contribute by about 20% to its global budget (Singh et al., 1995). However, the distinction between primary and secondary emissions is rather difficult, therefore the primary emissions of acetone have been neglected here.

The height of the planetary boundary layer (PBL) is taken equal to 500 m during daytime (Kallos, G., pers. comm., 2000) and 86 m (± 61 m) during nighttime. The nighttime PBL height has been derived from the observed decrease in O_3 that has been attributed to a deposition velocity of 0.5 cm s^{-1} (Galbally and Roy, 1980). Dry deposition of all isoprene and terpenes oxidation products described in the model is taken equal to 0.1 cm s^{-1} , except aldehydes and organic hydroperoxides (0.2 cm s^{-1}), organic acids and ozone (0.5 cm s^{-1}). For H_2O_2 and HNO_3 a value of 1.0 cm s^{-1} was adopted due to the highly humid forested environment corresponding to the deposition velocities over water/wet surfaces (Poisson et al., 2000 and references therein). Wet deposition was neglected since no rain occurred during the studied periods. All non-radical products with at least 7 carbon atoms are considered as semi- or non-volatile, and partition between gas and aerosol phase. The partitioning coefficients used have been measured in chamber studies (Griffin et al., 1999) and are similar with those experimentally determined in the field (Kavouras et al., 1999). Species with high polarity are also expected to partition between gas and aerosol phase, even if they have <7 carbon atoms (but a molecular weight >140).

3. Results and discussion

To elucidate the build up of oxidants and carbonyl and carboxyl compounds in the PBL of Pertouli forest and analyse their budget with the focus on the natural versus anthropogenic contribution, we present the model results and we compare with observations when available for O_3 , HO_x , carbonyls and carboxylic acids. For CO, a mean CO production of $1.5\text{--}2.5 \text{ ppbv CO h}^{-1}$, mainly due to isoprene oxidation is calculated. The CO observations and the evaluation of the secondary source of CO at Pertouli forest are discussed in detail in the accompanying paper by Gros et al. (2002).

The calculated nighttime NO_3 levels are $<3 \text{ pptv}$ and most of the time well below 0.5 pptv as expected from the high-humid conditions in the Pertouli forest. Indeed, it is well established that NO_3 radical is fully scavenged under high relative humidity conditions (Gözl et al., 2001). Our calculations are also in agreement with the extremely low NO_3 levels measured in a forested site of Portugal during the FIELDVOC 1994 experiment (Gözl et al., 2001). Therefore, NO_3 chemistry is not expected

to significantly affect the nighttime chemistry during the AEROBIC 1997 experiment.

3.1. Ozone

The ozone concentration calculated by the model is shown in Fig. 1a for the “basic” simulation (upper line) and the “ O_3 -no-transport” simulation (lower line, in which the O_3 concentration has been fixed to the observed value only in the beginning of the simulation). It can be seen that during nighttime ozone concentration decreases rapidly and reaches almost zero, mainly due to the absence of any photochemical production and the elevated loss of ozone not only by dry deposition but also by reaction with NO and unsaturated VOC. In the early morning, air masses enriched in ozone enter the boundary layer from the free troposphere and provide the observed rapid increase in O_3 concentration. This phenomenon occurs simultaneously with the beginning of the photochemical production of ozone and dominates in the morning. The maximum ozone concentration occurs in the afternoon and coincides with high net photochemical production of O_3 .

Indeed, the photochemical reactions incorporated into the model to describe the PBL chemistry at Pertouli forest cannot predict the rapid increase in the ozone concentration observed in the early morning hours. To estimate the amount of ozone that enters the boundary layer in the morning, the “ O_3 -no-transport” simulation is compared with the “basic” one. The difference thus calculated corresponds to the amount of ozone that is being transported to the PBL. During the 2nd intensive period, the daytime difference between the two simulations maximises at about 40–65 ppbv. Therefore, from the total ozone concentration measured in the PBL, the amount produced photochemically during the day is small and can maintain a maximum of only about 20 ppbv during day, which is only 23–61% of the observed O_3 maximum. On the contrary, during the 1st and particularly the 3rd intensive periods, the photochemical production appears to be the main source of ozone in the PBL. This might be because of the lower relative humidity during the 3rd intensive compared to the first two intensive periods, and therefore of the reduced photochemical loss of O_3 by photodissociation and subsequent reaction of O^1D with H_2O . In addition, the 3rd intensive is characterised by higher NO_x levels than the 1st intensive and moderate VOC levels, corresponding thus to a regime of higher O_3 production efficiency. During the 3rd intensive the contribution of chemistry to O_3 levels maximises (about 80–96% of the total observed O_3 maximum).

To evaluate the rate of ozone chemical production the “basic” simulation has been used to calculate the hourly changes in ozone mixing ratios due to photochemistry (Fig. 1b). From this figure it can be noticed that the O_3

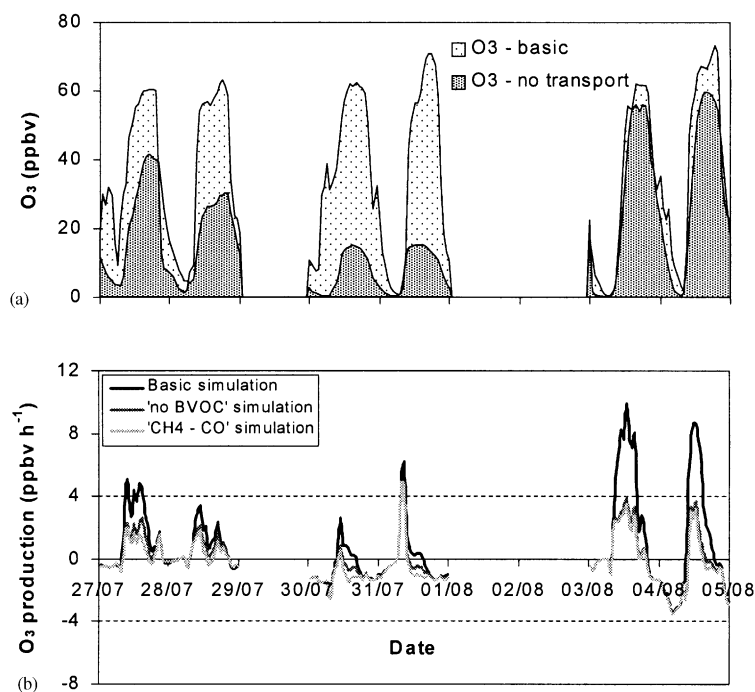


Fig. 1. (a) Calculated mixing ratios of O₃ for the “basic” and the “no-transport” simulations during the three intensive periods. The total area represents the ozone at the specific time (x-axis). The double shaded area represents the ozone resulting from transport and the single shaded area that locally produced by photochemistry. (b) Calculated net photochemical production of O₃ in ppbv h⁻¹ on an hourly basis when considering the oxidation of all VOC (basic), neglecting BVOC oxidation (no BVOC) and neglecting all non-methane VOC oxidation (CH₄-CO).

net photochemical production (O₃NPP) during daytime may exceed 8 ppbv O₃ h⁻¹, and the ozone net chemical loss due to chemical destruction of ozone by reaction with unsaturated VOC and NO in the absence of photochemical production in the evening. Although the diurnal pattern of O₃NPP is qualitatively reproduced during the whole studied period, some particularities are observed from one day to the other. For instance, on 30 and 31 July the strongest O₃NPP is calculated to occur during the morning hours instead of the generally observed early afternoon maximum. This disparate figure has been also calculated by Carslaw et al. (2001) (hereafter abbreviated as NC). Direct comparison between the two studies is hard to be made since different approaches were used to assimilate the observations and correct for non-measured photolysis rates and different periods were studied. Noticeable concept differences are (i) consideration of both α - and β -pinene in our study instead of only α -pinene by NC, (ii) use of JNO₂ here to correct the calculated photolysis rates of species other than NO₂ and O₃, whereas NC used JO¹D for this purpose, leading to slightly longer intensive photochemistry period during daytime in our simulations than in NC, (iii) use of different heterogeneous removal rates (e.g. higher γ coefficient for HO₂

here than in NC), (iv) use of the hourly O₃ concentration change calculated by the model and the amount hourly deposited to evaluate the net photochemical production of O₃ (here) instead of adding up the various chemical production and destruction terms (NC). The maximum O₃NPP thus calculated corresponds to the most intensive photochemistry days of 3 and 4 August of about 10 ppbv h⁻¹ which is 2 times lower than the 20 ppbv h⁻¹ calculated by Carslaw et al. (2001). This difference of a factor of 2 integrates all uncertainties in model calculations.

To evaluate the contribution of natural relative to the anthropogenic VOC, the O₃NPP has also been derived as explained above by using the results of the no-BVOC (neglecting BVOC chemistry) and the ‘CO + CH₄’ simulations (neglecting all non-methane VOC chemistry, Fig. 1b). By comparing the three estimates, we notice that up to 60% of the O₃NPP originates from BVOC oxidation, the maximum contribution calculated for the 3rd intensive with important NO_x levels but moderate VOC and CO levels. The contribution of the other NMHC is <0.3 ppbv h⁻¹. The contribution of the methane and CO chemistry is significant on 31 July early in the morning, when up to 4.5 ppbv O₃ h⁻¹ can be produced photochemically from CO and CH₄ oxidation

probably due to strong pollution sources both of NO and CO. Note that a very small part of the CO observed during the experiment and assimilated in the model is chemically produced from the reactive VOC. This is not expected to significantly modify the calculated hourly chemical O₃ production and the above given natural to anthropogenic contributions of VOC.

3.2. Odd hydrogen (HO_x = OH + HO₂)

The AEROBIC 1997 experiment provides an excellent opportunity to test the ability of the model to simulate HO_x budget, since OH and HO₂ radicals have been measured (Creasey et al., 2001) during this campaign. Analysis of HO_x data and extensive comparison to model results have been reported by Carslaw et al. (2001). However, the two model approaches significantly differ as explained in the previous section. Although both studies have difficulties in reproducing the observed HO_x levels, we can notice the importance of the activity coefficients of HO₂, which differs in the two studies (in this work γ_{HO_2} taken equal to the maximum reported value). The present study reproduces reasonably well the OH radical observations for all simulated days (Fig. 2a) although the calculated values fall in the lower observations and is better in reproducing the HO₂ observations on 31 July (Fig. 2b). For HO₂ there is an

important discrepancy on 27 July (Fig. 2b) when the measured concentrations of HO₂ are highly variable reflecting the very short lifetime (a few seconds) of this radical that follows therefore rapidly the short-term variations in solar irradiance. Such short-period changes are not simulated in our model since the photolysis rates are changing on an hourly basis. In addition, Carslaw et al. (2001) pointed out that the accuracy of the OH measurements is much better than that of HO₂ observations that might be also subject to artefacts induced by the presence of H₂O vapour. The impact of BVOC and of other non-methane VOC on HO_x budget has been investigated by the same simulations used to analyse O₃ budget as depicted in Fig. 2. BVOC reduce the maximum daytime OH levels by roughly $1\text{--}7 \times 10^6 \text{ rad cm}^{-3}$, whereas the other non-methane VOC deplete OH only by $0.1\text{--}3 \times 10^6 \text{ rad cm}^{-3}$ depending on the studied day. On the contrary, BVOC oxidation increases HO₂ daytime maximum by roughly $0.3\text{--}1.4 \times 10^8 \text{ rad cm}^{-3}$, whereas the other non-methane VOC, mainly anthropogenic, have a minor impact ($<0.4 \times 10^8 \text{ rad cm}^{-3}$ during daytime).

3.3. Carbonylic compounds

To simulate the temporal evolution of carbonyl compounds, the mixing ratios of HCHO, CH₃CHO

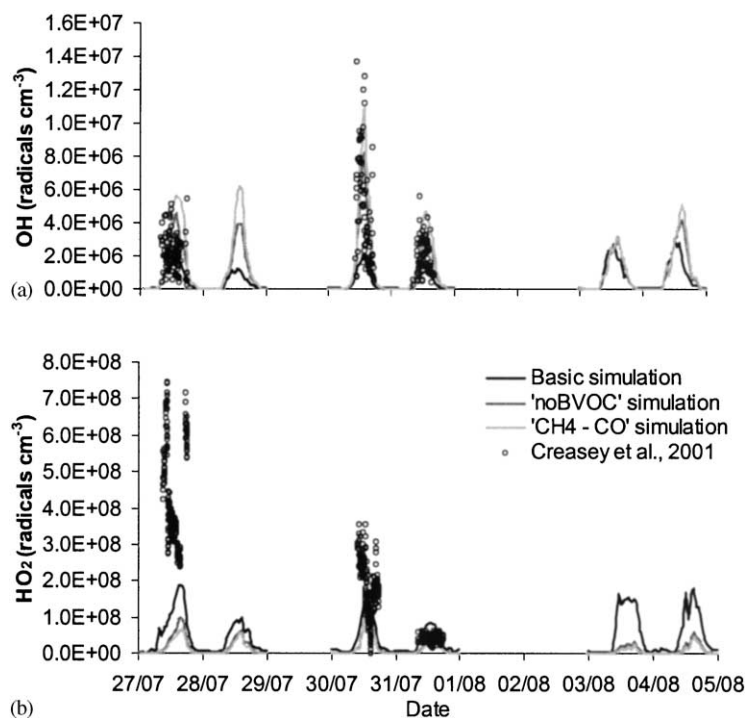


Fig. 2. Calculated concentrations of OH (a) and HO₂ (b) for the basic simulation during the three intensive periods (for line explanations see Fig. 1 caption), and comparison with measurements (open circles, Creasey et al., 2001).

and CH_3COCH_3 were fixed in the beginning of the simulation, and after that the model computed them taking into account their chemical production and loss and their dry deposition. The calculated mixing ratios for the three different chemical simulations are depicted in Fig. 3. We can see a well-defined diurnal variation with maximum in the early afternoon resulting from high chemical production and relatively low destruction at that time, and minimum during night when no photochemical production occurs and the destruction through dry deposition and reaction with NO_3 radicals is important. The production of aldehydes through ozone reaction during nighttime is negligible, because of the very low ozone concentration. Unfortunately, there are no reported observations of these compounds at the Pertouli forest to validate our model results. However, the calculated values of HCHO and CH_3CHO and their diurnal variation are comparable with observations

elsewhere. In rural areas, HCHO observations range from 0.1 to 6.5 ppbv (Khare et al., 1997 and references therein). The levels of 0.5–3 ppbv HCHO and of below 1 ppbv CH_3CHO observed by Kesselmeier et al. (2000) in a tropical forested site are in good agreement with our results. HCHO calculated values are also in the range of the 1–9 ppbv of HCHO measured in a Eucalyptus forest in Portugal (Trapp et al., 2001).

Comparison of the three simulations (Fig. 3) indicates that most of the chemically formed HCHO (up to 90% during daytime) and significant amounts of CH_3CHO (up to 40% during daytime) are produced by the oxidation of isoprene. Due to the chemical structure of terpenes, their decomposition in particular the H-abstraction path of their degradation by OH radicals is a chemical source of acetone as has been verified in chamber experiments (Aschmann et al., 1998). These results have been included in the chemical scheme of the

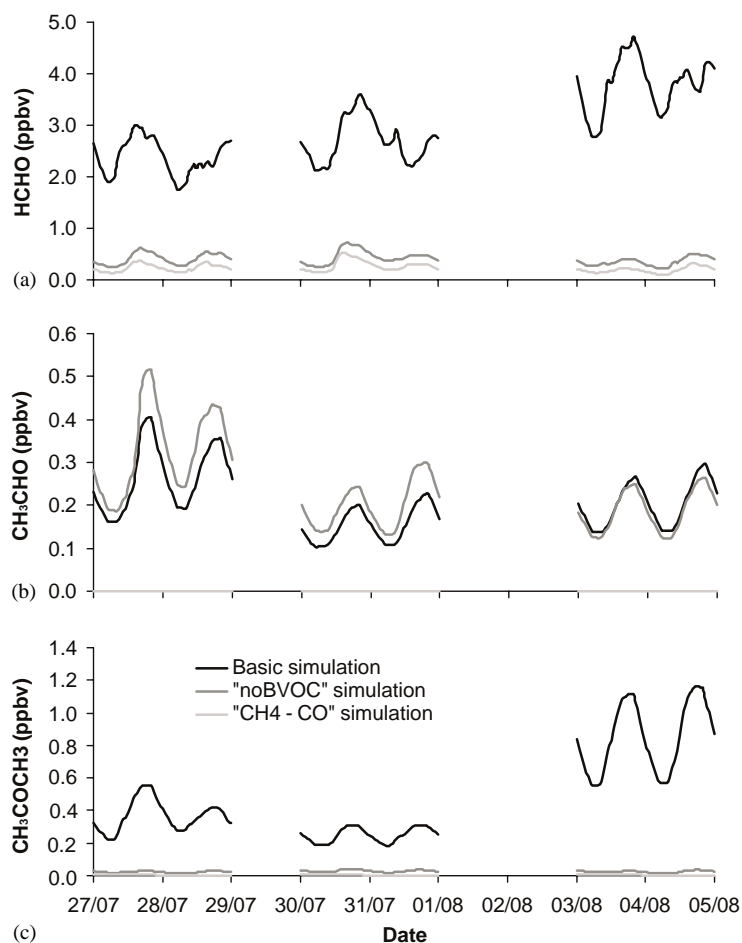


Fig. 3. Calculated mixing ratios of HCHO (a), CH_3CHO (b) and CH_3COCH_3 (c) during the three intensive periods. For line explanations see Fig. 1 caption.

model, although related with high uncertainty. According to our calculations up to 0.6 ppbv of acetone (mean value of 0.1 ppbv) is chemically produced per ppbv of α - and β -pinene oxidised in the area. The maximum acetone production rate of 0.11 ppbv h^{-1} has been calculated to occur during the highest photochemical activity period (noon of 4 August), when the photochemical production of O_3 is also elevated and the relative humidity is relatively low.

3.4. Carboxylic compounds

Organic acid formation in forested areas is also a topic of particular interest for the quality of the environment, since light organic acids can contribute to the rain acidity under certain circumstances. HCOOH and CH_3COOH have also primary emissions except of their chemical production, mainly by radical–radical reactions. Recent studies by Glasius et al. (2001) based on radiocarbon analysis showed that 80–100% of these acids observed in remote areas over Europe are of biogenic origin (primary or secondary). The mixing ratios of these acids are calculated taking into account their primary emissions, and compared well with the observations at Pertouli forest as shown in Fig. 4. On the basis of constant primary emissions (Section 3.2) and temporally variable chemical production and loss terms, the model simulates reasonably well the diurnal varia-

tion of these acids, especially that of formic acid, but with a smaller amplitude than observed. This small discrepancy may be related to opening of the PBL when the early morning air masses not affected by nighttime deposition and rich in organic acids enter the boundary layer and thus increase the acids abundances. This might explain the early morning peaks that appear in the measurements and are not simulated by the model. These peaks during the 3rd intensive are very small, pointing out a less important contribution of transport relative to the local photochemistry and emissions to the local budget of these acids, in line with the ozone observations during the same. BVOC chemistry increases almost by a factor of 2 and the calculated mixing ratios show the importance of secondary to primary emissions in this site.

3.5. Organic aerosols

As earlier discussed BVOC oxidation may lead to organic aerosol formation. In particular, the abundant forested environment pinenes can produce condensable oxidation products that form SOA in the area. This process is included in the model as described in Sections 2.1 and 2.2. According to our calculations, the oxidation of BVOC is increasing the organic aerosol concentrations by about $0.3\text{--}2.5 \mu\text{g m}^{-3}$ due to SOA formation that is 9–38% of the observed total organic aerosol

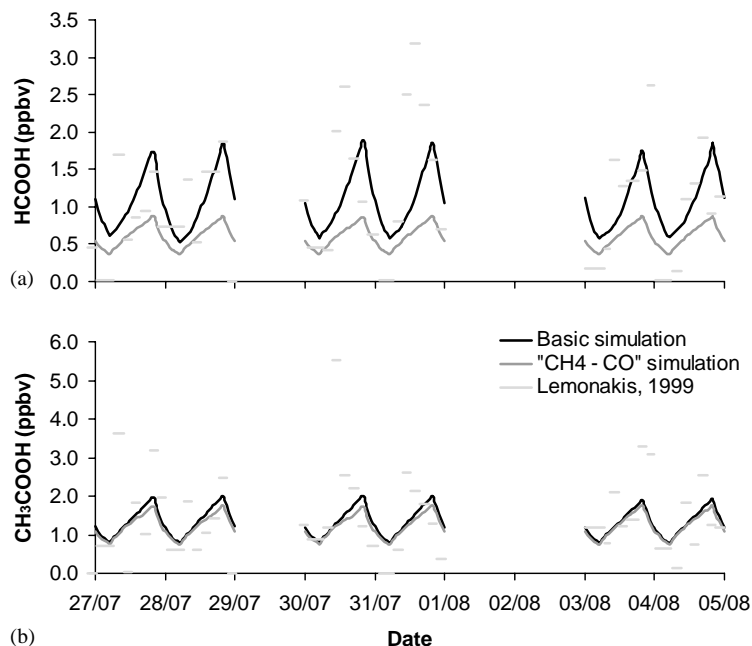


Fig. 4. Calculated mixing ratios of HCOOH (a) and CH_3COOH (b) for the "basic" simulation (black line) and the "no BVOC" simulation (grey line) during the three intensive periods and comparison with observation (short lines, Lemonakis, 1999).

levels (mean value of $10.4\mu\text{g m}^{-3}$). The remaining organic carbon can be attributed to primary sources, anthropogenic VOC oxidation, regional chemical production and long-range transport. Therefore, BVOC can be an important source for SOA in forested areas under favourable photochemical conditions.

4. Conclusions

A chemical box model able to simulate α - and β -pinene and isoprene photochemistry in the troposphere has been used to evaluate the impact of BVOC on the chemical composition of the boundary layer in a valley-forested site of central Greece studied during the AEROBIC field campaign in July–August 1997. Only 23–61% of the observed ozone (O_3) mixing ratios can be attributed to the local photochemistry during the first part of the experiment, whereas this contribution increases to 80–96% during the second part of the campaign when the photochemical production of O_3 is calculated to be up to 10ppbv h^{-1} with the maximum rates in the morning and in the late afternoon. The remaining part of O_3 is reaching the boundary layer by penetration from the free troposphere during the morning opening of the valley. BVOC oxidation is shown to be an important source of carbonyl compounds and organic acids, in particular, contributing 1.5–4.3, 0.2–1.1 and 0.1–1 ppbv to the daytime ambient levels of formaldehyde, acetone and formic acid, respectively. BVOC are able to significantly contribute (up to 38%) to the observed total organic aerosol levels and to produce up to about $2.5\mu\text{g m}^{-3}$ of SOA under favourable photochemical conditions.

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